



Research papers

On the use of coprostanol to identify source of nitrate pollution in groundwater



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ABSTRACT

Investigation of contaminant sources is indispensable for developing effective countermeasures against nitrate (NO_3^-) pollution in groundwater. Known major nitrogen (N) sources are chemical fertilizers, livestock waste, and domestic wastewater. In general, scatter diagrams of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ from NO_3^- can be used to identify these pollution sources. However, this method can be difficult to use for chemical fertilizers and livestock waste sources due to the overlap of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ ranges. In this study, we propose to use coprostanol as an indicator for the source of pollution. Coprostanol can be used as a fecal contamination indicator because it is a major fecal sterol formed by the conversion of cholesterol by intestinal bacteria in the gut of higher animals. The proposed method was applied to investigate NO_3^- pollution sources for groundwater in Shimabara, Nagasaki, Japan. Groundwater samples were collected at 33 locations from March 2013 to November 2015. These data were used to quantify relationships between NO_3^- -N, $\delta^{15}\text{N}$ - NO_3^- , $\delta^{18}\text{O}$ - NO_3^- , and coprostanol. The results show that coprostanol has a potential for source identification of nitrate pollution. For lower coprostanol concentrations ($<30 \text{ ng L}^{-1}$) in the nitrate-polluted group, fertilizer is likely to be the predominant source of NO_3^- . However, higher concentration coprostanol samples in the nitrate-polluted group can be related to pollution from livestock waste. Thus, when conventional diagrams of isotopic ratios cannot distinguish pollution sources, coprostanol may be a useful tool.

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1. Introduction

Nitrate contamination in groundwater as a consequence of intensive agricultural activities is a severe problem. In order to establish effective countermeasures against nitrate contamination identification of the nitrate source is crucial. Statistical methods such as correlation between nitrate and characteristic ions (e.g., SO_4^{2-} , Ca^{2+} , and Mg^{2+}) have been successfully used to locate and understand nitrate sources. Positive correlation with such ions means that the nitrate source originates from chemical fertilizer (Babiker et al., 2004). In a similar manner, stable isotopic ratios of nitrate ($\delta^{15}\text{N}$) have been applied as a powerful tool (e.g., Williams et al., 1998; Rivers et al., 1996). Although, $\delta^{15}\text{N}$ from nitrate sources shows a distinct range (e.g., -15 to $+15\text{‰}$ in atmospheric NO_3 , -4 to $+4\text{‰}$ in inorganic fertilizer, $+2$ to $+30\text{‰}$ in organic fertilizer, and $+10$ to $+20\text{‰}$ in animal waste; Kendall, 1998), it is often difficult to distinguish pollution sources due to

overlapping ranges. The $\delta^{18}\text{O}$ from nitrate, however, is an additional tool for determining nitrate source and reactions. Kendall (1998) illustrated the usefulness of scatter diagrams of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ for interpreting dominant nitrate sources. He showed that different ranges could be explained by the diverse origins of nitrate (NO_3 in precipitation, desert NO_3 deposits, NO_3 fertilizer, NH_4 in fertilizer and rain, manure and septic waste, and soil N). Moreover, dual isotopic data are useful for judging if denitrification occurs because this process increases the $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of residual nitrate. Although, nitrate originating from nitrate fertilizer or atmospheric sources are distinguishable from ammonium fertilizer, soil N, and manure containing $\delta^{18}\text{O}$, it is still difficult to distinguish different sources of chemical fertilizer and livestock waste sources because of overlapping $\delta^{15}\text{N}$ ranges. To overcome this problem, isotopic data combined with a Bayesian mixing model is a reliable way for quantifying proportional contributions of potential nitrate sources (Matiatos, 2016; Kim et al., 2015). However, precaution is required because the model resolution is significantly affected by the temporal variability of the isotopic composition of nitrate

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in the mixture and uncertainty of the isotopic composition of different nitrate sources (Xue et al., 2012).

Shimabara City, Nagasaki, Japan, utilizes groundwater for agriculture, industry, and domestic water including drinking water. However, due to intensive agricultural activities, the nitrate level in groundwater has increased to above the Japanese drinking water quality standard (10 mg L^{-1}). According to Nakagawa et al. (2016), 38% (15 out of 40 groundwater wells) exceed the permissible $\text{NO}_3\text{-N} + \text{NO}_2\text{-N}$ concentration. The nitrate pollution in groundwater has been shown to be related to chemical fertilizer and livestock waste by use of the correlation matrix for major dissolved ion components. However, the identification of specific nitrate sources could not be accomplished in the above study. For this reason, we herein propose an easy-to-use approach involving coprostanol to identify the main nitrate source. Coprostanol (5β (H)-Cholestan-3 β -ol, CAS No. 360-68-9) is one of the sterols, which is produced by bacterial reduction of cholesterol in the gut of higher animals (Martins et al., 2007). It has been widely used as an indicator of fecal contamination in lagoons and estuaries (Martins et al., 2007; Reeves and Patton, 2005). In this paper, $\text{NO}_3\text{-N}$, coprostanol, $\delta^{18}\text{O}$, and $\delta^{15}\text{N}$ from nitrate were investigated to evaluate the feasibility of the proposed methodology to identify the source of nitrate groundwater pollution. For this purpose, three kinds of relationships were developed and analyzed; (i) $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ from nitrate derived from Kendall (1998), (ii) $\delta^{15}\text{N}$ from nitrate and coprostanol, and (iii) $\text{NO}_3\text{-N}$ and coprostanol levels.

2. Study site

Shimabara City is located on the northeastern Shimabara Peninsula, covering 82.8 km^2 (Fig. 1). In the northern part of the city, an alluvial fan is formed from Mt. Fugen located on the apex center of

the peninsula. Volcanic deposits such as tuff breccia, tuff, and volcanic conglomerate constitute and are distributed around the mountain. Upland areas and paddy fields are concentrated in the northern parts of the city. Areas above an altitude of 200 m are generally occupied by forest. Above an elevation of 300 m, hornblende-andesite is distributed. Due to the collapse of Mt. Mayu in 1792, Mayuyama avalanche debris deposits are distributed in the eastern area of the city. The urban area lies on these deposits. The climate is mild-humid with mean annual precipitation ranging between 1970 and 2476 mm and mean annual temperature between 16.9°C and 17.2°C (2013–2015). Although it rains throughout the year, the rainfall is particularly abundant from June to August.

3. Materials and methods

Groundwater samples were collected at 33 locations from March 2013 to November 2015 (Fig. 1). Sampling locations were constituted by 6 shallow wells, 21 deep wells, 1 unknown well depth, and 5 springs. Shallow well is defined as $<30 \text{ m}$ deep and deep well as $>30 \text{ m}$ deep. Collected water samples for analysis of NO_3^- and coprostanol were filled in prewashed bottles and stored in refrigerator. Samples for nitrate isotope ratios were filtered through $0.22 \mu\text{m}$ membrane filter and kept frozen until analysis. NO_3^- was analyzed by ion chromatography of suppressor type (Metrohm 861 Advanced Compact IC). $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate were determined by the denitrifier method (Casciotti et al., 2002; Sigman et al., 2001) for samples collected on November 4 and 20 2014 and November 20 2015. Denitrifying bacteria lacking N_2O reductase convert NO_3^- to N_2O . Analysis of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of induced N_2O were implemented simultaneously. Dual isotopes of nitrate can be analyzed accurately for samples that are affected

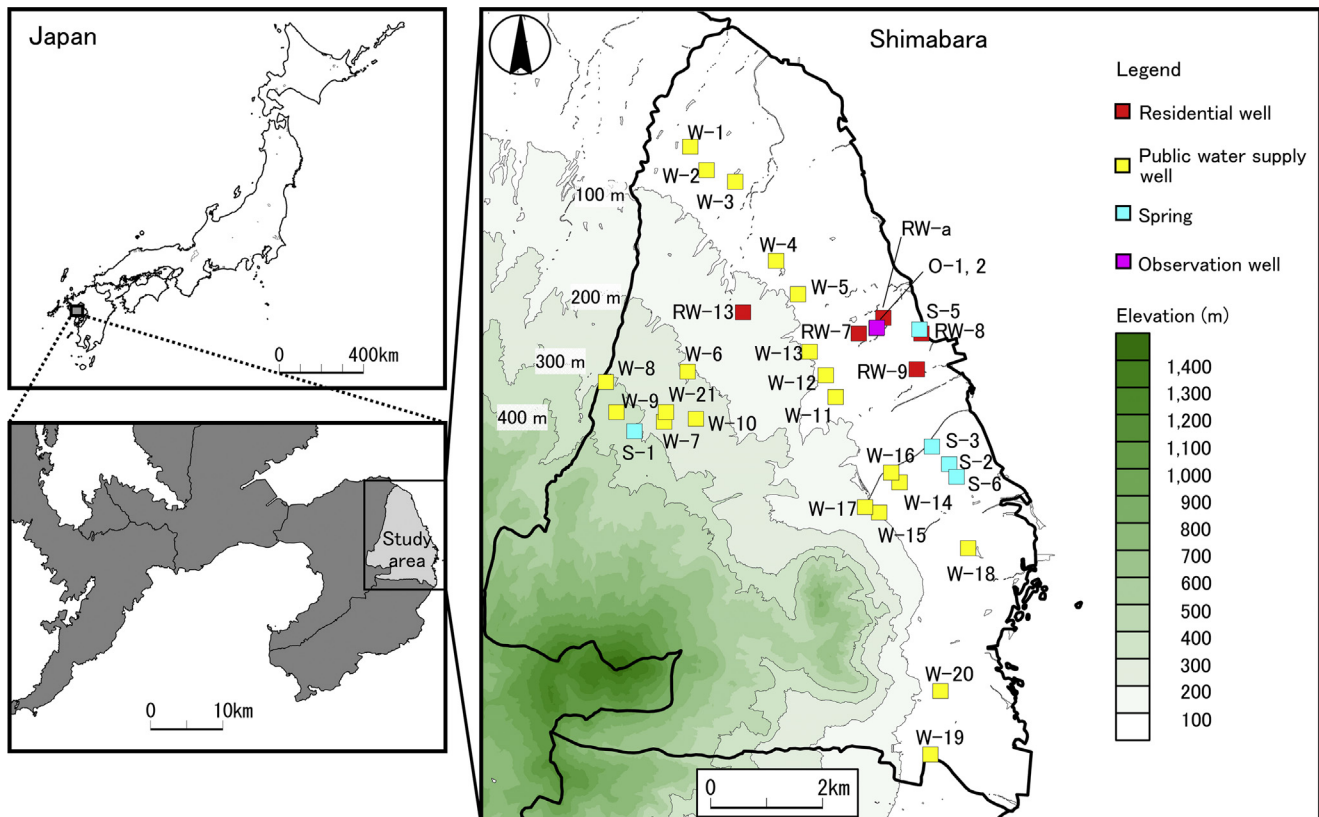


Fig. 1. Location of sampling sites.

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